Crystal structure of pentalanthanum bromotriindate, La_5In_3Br

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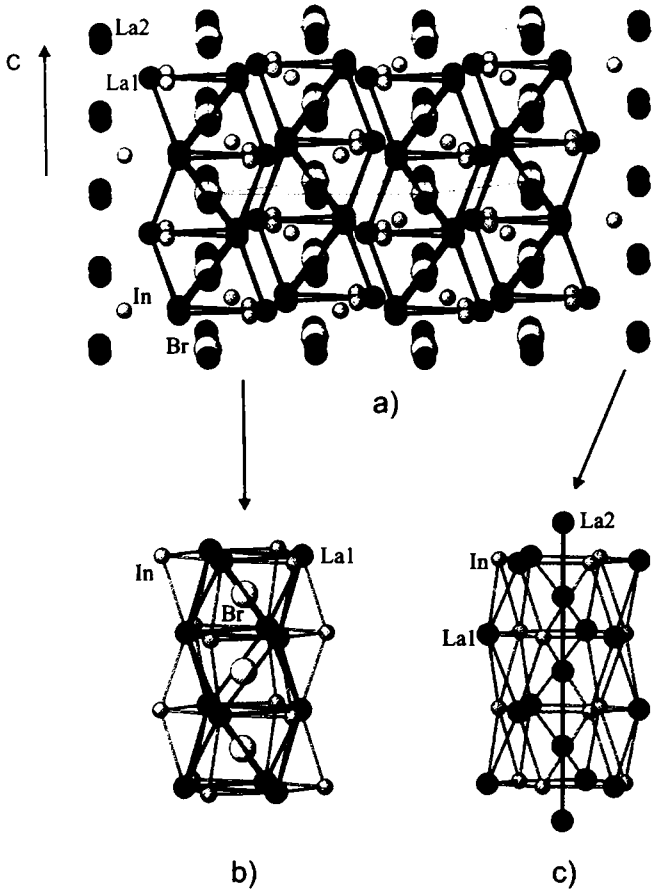

Abstract

$BrIn_3La_5$, hexagonal, $P6_3/mcm$ (No. 193), $a = 9.828(2)$ Å, $c = 6.829(3)$ Å, $V = 571.3$ Å^3, $Z = 2$, $R_{gt}(F) = 0.030$, $wR_{ref}(F^2) = 0.065$, $T = 293$ K.

Source of material

The title compound was synthesized from stoichiometric mixtures of La, $LaBr_3$ and In under Ar-atmosphere in a sealed Ta ampoule at 1173 K for 65 days. As the reactants and the product are air and moisture sensitive, all handling was carried out under Ar atmosphere inside a glove box or through the Schlenk technique.

Discussion

The Mn_5Si_3-type lattice is known to possess an amazing ability to host a large number of interstitials ranging from the main group elements B, C, N, O, Cl, Si, Br, I to transition metals Mn, Fe, Cu, Zn, Ag and Cd, among others [1-5]. These compounds, derived from the Nowotny phases [6-8], is exemplified by La_5Sn_3Br, which has 34 valence electrons [5]. Computational analysis demonstrated that the host lattice with La as the main component is very tolerant to the variation of the number of valence electrons [5]. This has led us to attempt the synthesis of La_5In_3Br, which is the first compound with a lanthanide as the first component and a group 13 element as the second. The number of valence electrons of 31 is still within the bonding range of the host framework [5]. In this contribution we present the single crystal structure of La_5In_3Br. As described elsewhere [2,5], the structure consists of face- sharing La_6 octahedron chains parallel to the *c*-axis (see figure). These octahedra of La1 are centered by the Br species and surrounded by type 2 La (La2) and the In atoms. La2 forms chains, also parallel to the *c*-axis, in the channels between these La_6 octahedron chains. The La2—La2 and La1—La2 distances are 3.414(2) Å and 4.029(1) Å, respectively. The latter is shorter than the La1—La1 distances of 4.302 Å – 4.534 Å in the La_6 octahedron. The shortest La1—In distance is 3.351(2) Å. The La2—In distance is 3.4750(9) Å. Thus the primary metal-metal interaction is between La2 and La2, La1 and In, La1 and La2, La2 and In. The bonding pattern has been analyzed previously [2,5]. It is interesting to note that no La_5In_3 phase has been reported. The smaller number of valence electrons, as compared to that of La_5Sn_3 (Mn_5Si_3 type), is probably not enough for stability at least in the Mn_5Si_3 structure.

Finally, we should mention that many crystals of the title compound exhibit super-reflections that lead to the increase of the *a*- and *b*-axis lengths by a factor of $\sqrt{3}$.

Table 1. Data collection and handling.

Crystal:	metallic fragment, size 0.02 × 0.04 × 0.06 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	276.23 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	2288, 182
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 182
$N(param)_{refined}$:	14
Programs:	SHEXTL [9], SADABS [10]

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Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
La(1)	6*g*	0.2664(1)	0	1/4	0.0174(6)	0.0155(8)	0.067(1)	0.0077(4)	0	0
La(2)	4*d*	1/3	2/3	0	0.0490(8)	U_{11}	0.0177(9)	$U_{11}/2$	0	0
In	6*g*	0.3927(2)	*x*	1/4	0.0180(7)	U_{11}	0.116(2)	0.0096(7)	0	0
Br	2*b*	0	0	0	0.019(1)	U_{11}	0.066(3)	$U_{11}/2$	0	0

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